

Structure of Isotactic Polypropylene in Composites with Natural Fibres Obtained in Various Processing Methods

Abstract

The structure of composite polypropylene/natural fibres was investigated. The kind of processing techniques (injection and press methods) and kind of natural fibres (flax and hemp), as well as the form of lignocellulosic materials (long and cut fibres), influenced the supermolecular structure of the isotactic polypropylene matrix in composite systems. In the case of composites prepared by the injection method, a hexagonal form (β) of iPP besides the monoclinic (α) was created. The amount of the β phase in composites with flax fibres was higher compared to composites with hemp fibres. The content of this polymorph form was increased with fibre loading. The processing of some polypropylene without fibres by injection caused the generation of hexagonal form, but significantly less (~100%) in comparison to the composite materials. In samples prepared by press moulding, when pressure was applied, polypropylene crystallised in the monoclinic form only.

Key words: natural fibres, polypropylene, composites, polymorphism, structure, processing, pressure.

Introduction

The investigation and application of composite thermoplastic polymers such as isotactic polypropylene (iPP) with natural materials like wood or natural fibres (NF) is continually expanding. The growing interest in using lignocellulosic/thermoplastic composites is due to their many advantageous properties [1-4].

The manufacture of composites requires the consideration of many problems. One of the most important is the influence of the fibre-matrix adhesion on the materials' behaviour [5]. Poor adhesion between native natural fibres and polypropylene has been improved by chemically modifying the surface of fibres or by using maleic anhydride-polypropylene copolymers (MAH-PP) [6]. Other important factors are the processing conditions, such as temperature and pressure during extrusion and injection moulding [7-9]. For good impregnation of natural fibres by thermoplastic polymers, a higher temperature of processing is advantageous; this is connected with adequate polymer viscosity. On the other hand, the temperature of processing is limited by the thermal resistance of the lignocellulosic materials to between 210-230°C.

Moreover, we may observe the great influence of the processing parameters on the increase in the shearing forces during the formation of the composites. These forces may be caused by the polymorphic changes in the polypropylene matrix [11-13].

We have suggested earlier, that the reason for the creation of these different forms may be perturbations in the mobility of the chains during crystallisation [14, 15].

In our previous studies on composites of iPP with cut hemp or flax fibres, we mainly focused on mechanical properties and flammability [16, 17].

Investigations into the polypropylene composites with natural fibres evoke questions about difference and similarity in polypropylene structure prepared according to various kinds of processing methods, as well as different species of lignocellulosic materials.

Experimental

Materials

In this work, the supermolecular structures of polypropylene in the following composites were analysed:

- iPP/cut natural fibres (NFs) obtained by injection moulding process from granulate. The contents of NF were 5%, 7.5% and 10%.

- boards (100×100 mm) with cut and long natural fibres obtained by press moulding under pressure. The content of NF was 10%.

Hemp and flax were used as natural fibres. The fibres with lengths of 50-250 mm, (average 100-150 mm) were named as long fibres. The fibres cut into a mean length of 2-3 mm were named as cut fibres. In this work, NFs without any chemical modification were used.

Processing

Two methods of blending were employed:

- extruding in one screw extruder, with 25 mm, L/D= 25, operating at 30 rpm, temperature zones from 140 to 200°C. The composites obtained were granulated for subsequent forming by injection moulding. The following injection parameters were used: injection temperature 210°C, injection pressure 45 bar, and mould temperature 30°C.
- forming by press moulding. The samples were heated up to 200°C and cooled slowly. The pressure was retained during non-isothermal crystallisation whilst the temperature dropped to 50°C. We used a pressure of 2.94 MPa.

Structural analysis

The structural investigations of the samples were carried out by means of a wide-angle X-ray scattering method (WAXS), using CuK α radiation ($\lambda=1.5418$ Å). On the basis of separated diffraction lines [18-20], the β -phase content was analysed.

The amount of β -form (k) in samples of polypropylene composites was determined using the well-known Turner-Jones formula [21].

Results and discussion

In the present study, we have considered structural investigations on samples obtained during injection moulding and press moulding.

The WAXS examination showed that on the surface of all the samples obtained by the injection moulded process, the pseudo-hexagonal β -phase was noted as well as the monoclinic α -one (Figures 1 and 2). The peak at $2\theta=16, 12^\circ$ confirms the presence of the β -form in the sample investigated.

In our earlier studies we assumed, from the geometrical point of view, that the hexagonal β -form is a transitory form

between the melt phase and the monoclinic form [13]. Shear forces point and accelerated crystallisation [22] as a factor stimulated the orientation of macromolecules. The temperature at which the process proceeds in the presence of shear forces is important. The lower the temperature at which the fibres undergo these forces, the greater the amount of the β -form in polypropylene matrix [10].

The content of the hexagonal β -form (k) as a function of amount of the hemp and flax fibres is presented in Figure 3.

The applied conditions of the injection moulding process causes a rise of 16% of the β -form in the polypropylene samples without fibres (the bottom curve on Figure 3). The presence of only 5% of fibres in the composite causes a rise of over 25% of the β -form in the crystalline phase of the polypropylene matrix. As shown on the diagram, the difference between composites with flax and hemp are not sig-

nificant, but in all samples the presence of cut flax fibres causes an increase in β -form (by about 6-20%) in comparison to the composites containing cut hemp fibres.

In conclusion, the appearance of the shearing forces depends on the quantity of cut fibres in the composite and the kind of fibres (the difference between hemp and flax) for samples obtained under the same processing conditions.

The β -form is not present in the structure of the polypropylene matrix in the composite boards manufactured under pressure conditions (Figure 4).

This phenomenon is observed in composites with both long and cut hemp and flax fibres. There are no significant differences between the structure of the polypropylene matrix in the samples obtained using long (the bottom curves) or short (the upper curves) natural fibres.

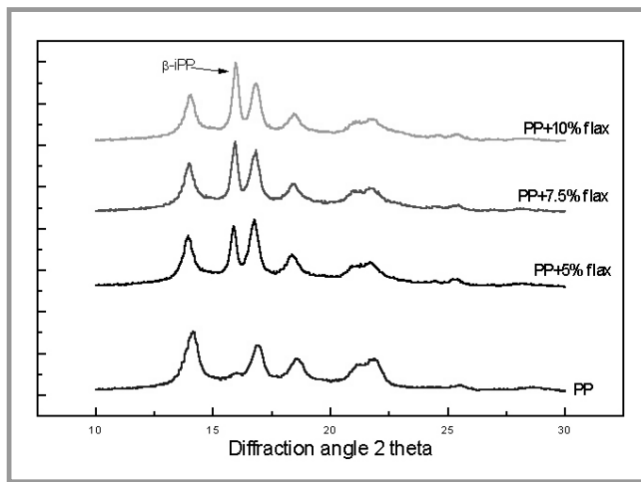


Figure 1. X-ray diffraction pattern of flax/PP composites obtained by the injection method.

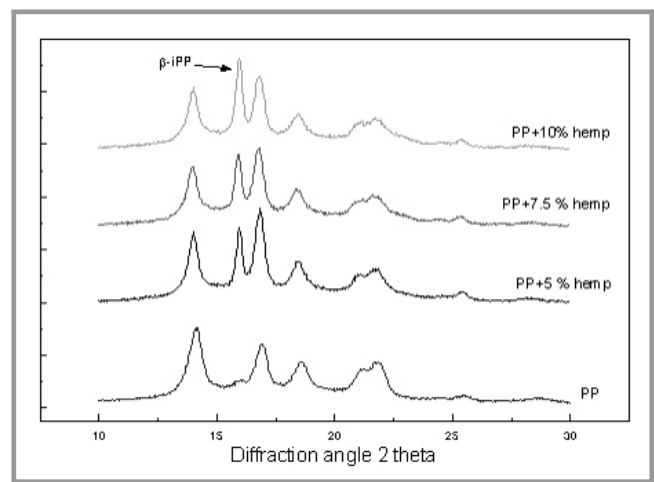


Figure 2. X-ray diffraction pattern of hemp/PP composites obtained by the injection method.

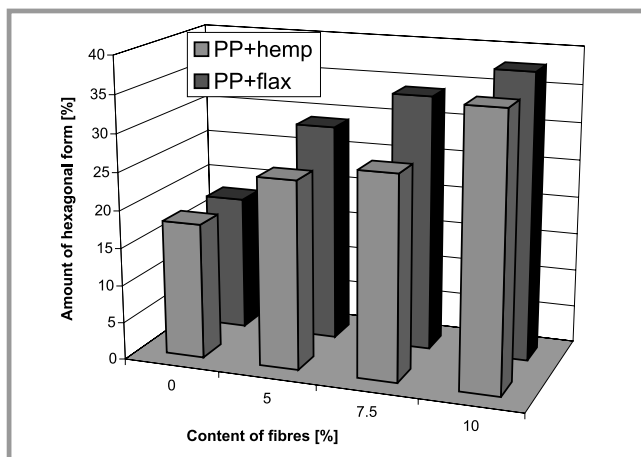


Figure 3. Amount of the hexagonal form of iPP vs. content of fibres.

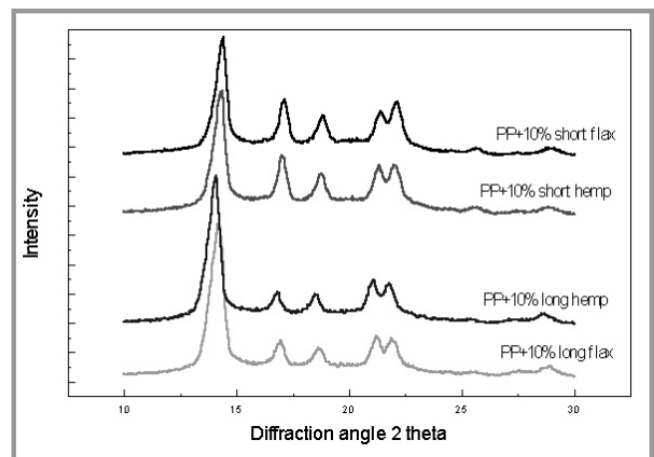


Figure 4. X-ray diffraction pattern of hemp/PP composites obtained by the press method.

The composites obtained by compression moulding contain the monoclinic form of iPP only because the shear forces are not present. Moreover, according to the statement given earlier, the elevated uniaxial pressure reduces the creation of hexagonal forms. The uniaxial stress (the action of pressure) on the melted polypropylene sample may force a screw motion of helical chains in a direction perpendicular to the direction of the applied press. The screw motions of the layers of polypropylene chains lowers the barrier energy of the $\beta \rightarrow \alpha$ phase transition [23]. Therefore, in composites obtained under pressure, due to the action of stress, the formation of the monoclinic a-form is preferable.

Conclusions

The supermolecular structure of isotactic polypropylene in composite materials has been investigated in the context of the influence of processing technique kind and the form of the fibres.

The results described in this work show that the factors indicated above determined the polymorphic changes of the polypropylene matrix.

Because the b-phase in injection moulded samples only was noted, the factor causing this form to occur must be the shearing forces. The amount of hexagonal phase depends on the content of lignocellulosic materials and on the kind of fibres (flax or hemp).

In press moulding, when applied to pressure only, the occurrence of the a modification in composites is preferable. □

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